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(54) Dielectric ceramic compositions and dielectric resonators

(57) The present invention provides dielectric ceramics with less variation of temperature coefficient at a resonant frequency due to heating history during the sintering of $ZrTiO_4$ and $ZrO_2 - SnO_2 - TiO_2$ ceramics, and having a high unloaded Q value and a high dielectric constant, and a temperature coefficient at a resonant frequency which is widely variable as desired, and dielectric resonators using the dielectric ceramics which have a high unloaded Q value and a strong electrode layer. The main components of the dielectric ceramics (2) and (5) may be expressed by the formula: $xZrO_2 - yTiO_2 - zA_{(1+u)/3}B_{(2-u)/3}O_2$ wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, B denotes at least one component

selected from the group (B) consisting of Nb and Ta, and x, y, z and u (x, y and z are molar fractions and u is a value within the range from 0 to 1.90) have the relation of $x + y + z = 1.0$, $0.10 \leq x \leq 0.60$, $0.20 \leq y \leq 0.60$, $0.01 \leq z \leq 0.70$. The main component may include, as accessory components, at least one component selected from the group (C) consisting of Ba, Sr, Ca, Cu, Bi and W at 0.005 to 7.000 % by weight of the entire weight of the ceramic. According to the cylindrical coaxial dielectric resonator, electromagnetic waves are incident in the direction of an opening end (3) and a necessary output is obtained from electrodes (1) and (4) by using the TEM mode.

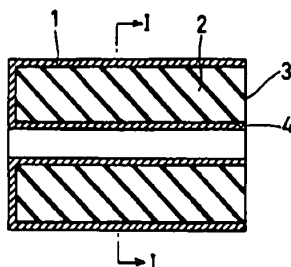


FIG. 1A

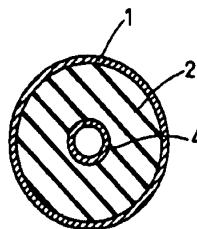


FIG. 1B

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Description

This invention relates to dielectric ceramics and dielectric resonators for use in such high-frequency ranges as microwave and millimeter-wave frequencies.

Recently, dielectric ceramics have been widely used in dielectric resonators and filters in microwave and millimeter-wave frequencies at wavelengths of several centimeters or less (hereinafter referred to as microwave in general). It is required that a dielectric material for use in such applications have a high unloaded Q (Q_u) value and dielectric constant ϵ_r , and that the temperature coefficient at a resonant frequency τ_f be variable as desired. The Q value is the inverse of an inductive loss $\tan \delta$.

Various materials appropriate for use in such applications have been conventionally reported, among which ZrTiO₄ ceramics are included. Also included in such materials are ZrO₂-SnO₂-TiO₂ ceramics, the ZrO₂-SnO₂-TiO₂-MgO ceramic suggested in Japanese Laid-Open Patent No. 62-132769 and the ZrO₂-SnO₂-TiO₂-CoO-Nb₂O₅ ceramic in Japanese Laid-Open Patent No. 2-192460, for example.

However, although the ZrTiO₄ ceramics according to the prior art have a high dielectric constant of 45, the temperature coefficient at a resonant frequency is high in the positive side at 54ppm/°C, and the temperature coefficient at a resonant frequency is significantly varied by the heating history during sintering. The ZrO₂-SnO₂-TiO₂ ceramic has achieved a low temperature coefficient of about 0ppm/°C at a resonant frequency, but the variation of temperature coefficient at the resonant frequency caused by the heating history causes problems. In addition, conventional materials have such problems that the dielectric constant and unloaded Q value are low, and that the temperature coefficient at a resonant frequency cannot be varied as desired. Further, in the case of application to a coaxial resonator having electrodes formed on the surface of the dielectric ceramic, a planar filter and the like, there are problems in that the resonant frequency is easily deviated and the unloaded Q value is decreased when the bond strength of the electrode layer to the dielectric ceramic is low.

The object of the present invention is to provide ZrTiO₄ and ZrO₂-SnO₂-TiO₂ ceramics with less variation of temperature coefficient at a resonant frequency due to heating history during sintering.

It is another object of the present invention to provide dielectric ceramics that have a high unloaded Q value and a high dielectric constant, and have a temperature coefficient at a resonant frequency which is variable as desired.

It is still another object of the present invention to provide dielectric resonators which comprise strong electrode layers having a high unloaded Q value. The subject of the present invention is to achieve one of these objects or to achieve more than two objects at the same time.

In order to achieve the objects described above, the present invention provides a dielectric ceramic comprising as the main component a complex oxide formed of both Zr and Ti, at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, and as the accessory components at least one component selected from the group (C) consisting of Ba, Sr, Ca, Cu, Bi and W.

For the present dielectric ceramic, it is preferred that the main component of the dielectric ceramic is expressed by the Formula: $x\text{ZrO}_2 \cdot y\text{TiO}_2 \cdot z\text{A}_{(1+u)/3}\text{B}_{(2-u)/3}\text{O}_2$, wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, B denotes at least one component selected from the group (B) consisting of Nb and Ta, and x, y, z and u are present within the range expressed by Formula 1, wherein x, y and z denote molar fractions and u denotes a value expressed by the Formula 1.

$$x + y + z = 1$$

$$0.10 \leq x \leq 0.60$$

$$0.20 \leq y \leq 0.60$$

$$0.01 \leq z \leq 0.70$$

$$0 \leq u \leq 1.90$$

Formula 1

According to the dielectric ceramic, it is preferred that the accessory components of the dielectric ceramic are present within the range of 0.005 to 7.000 % by weight based on the entire weight of the ceramic. The amount of the accessory component is the weight of an oxide form in which the component is present in the ceramic, and is a value which is changed into {BaO, SrO, CaO, CuO, Bi₂O₃, WO₃}.

Further, it is preferred that the main component comprises a ZrTiO₄ or crystallographical ZrTiO₄ phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta.

Preferably, the main component comprises a ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, and a/b (a and b denote the total of molar fractions of the components A and B) ranges from 0.5 to 1.9.

For the present dielectric ceramic, it is preferred that the main component further comprises a complex oxide formed of at least one component selected from the group (D) consisting of Sn, Hf and Ge.

Preferably, the main component of the dielectric ceramic is expressed by the Formula: $x\text{ZrO}_2 - y\text{TiO}_2 - z\text{A}_{1/4 \dots 1/2}\text{B}_{1/2 \dots 1/4}\text{O}_2 - v\text{DO}_2$, wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, B denotes at least one component selected from the group (B) consisting of Nb and Ta, and D denotes at least one component selected from the group (D) consisting of Sn, Hf and Ge, and x, y, z, v, and u are present within the range expressed by Formula 2, wherein x, y, z and v denote molar fractions and u denotes a value expressed by the Formula 2.

$$x + y + z + v = 1$$

$$0.10 \leq x \leq 0.60$$

$$0.20 \leq y \leq 0.60$$

$$0.01 \leq z \leq 0.50$$

$$0.001 \leq v \leq 0.20$$

$$0 \leq u \leq 1.90$$

Formula 2

Further, it is preferred that the accessory components of the dielectric ceramic comprise at least one component selected from the group (C) consisting of Ba, Sr, Ca, Cu, Bi and W within the range from 0.005 to 7.000 % by weight based on the entire weight of the ceramic.

For the present dielectric ceramic, it is preferred that the main component comprises a ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, at least one component selected from the group (B) consisting of Nb and Ta, and at least one component selected from the group (D) consisting of Sn, Hf and Ge.

Preferably, the main component comprises a ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, at least one component selected from the group (B) consisting of Nb and Ta, and at least one component selected from the group (D) consisting of Sn, Hf and Ge, and a/b (a and b denote the total of molar fractions of the components A and B) ranges from 0.5 to 1.9.

The dielectric resonator of the present invention is characterized by a dielectric ceramic having the structure described above, and an electrode formed on the surface of the dielectric ceramic.

For the present dielectric resonator, it is preferred that the electrode is copper or silver.

In the structure of the present invention, the main component includes a complex oxide formed of both Zr and Ti, at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, and as the accessory components at least one component selected from the group (C) consisting of Ba, Sr, Ca, Cu, Bi and W. Consequently, the present invention provides dielectric ceramics with less variation of temperature coefficient at a resonant frequency due to heating history during the sintering of the ZrTiO_4 ceramic.

According to the preferred structure of the composition formula and the Formula 1, the present invention provides dielectric ceramics that have a high unloaded Q value and a high dielectric constant, and have a temperature coefficient at a resonant frequency which is variable as desired.

According to the dielectric ceramic expressed by the composition formula and the Formula 1, the main component comprises a ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta. Thus, the present invention provides dielectric ceramics having a higher unloaded Q value and a high dielectric constant, and is superior in thermo-stability at a resonant frequency.

According to the dielectric ceramic expressed by the composition formula and the Formula 1, the main component comprises a ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, and a/b (a and b denote the total of molar fractions of the components A and B) ranges from 0.5 to 1.9. Thus, the present invention provides dielectric ceramics having a much higher unloaded Q value and a high dielectric constant, and is superior in thermo-stability at a resonant frequency.

For the present dielectric ceramics, it is preferred that the main component further comprises a complex oxide formed of at least one component selected from the group (D) consisting of Sn, Hf and Ge. Thus, the present invention provides dielectric ceramics with less variation of temperature coefficient at a resonant frequency due to heating history during the sintering of ZrO_2 - SnO_2 - TiO_2 ceramics.

5 For the present dielectric ceramic expressed by the composition formula and the Formula 2, it is preferred that the main component comprises a ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, at least one component selected from the group (B) consisting of Nb and Ta, and at least one component selected from the group (D) consisting of Sn, Hf and Ge. Thus, the present invention provides dielectric ceramics having a higher unloaded Q value and a high dielectric constant, and is superior
10 in thermo-stability at a resonant frequency.

According to the dielectric ceramic expressed by the composition formula and the Formula 2, the main component comprises a ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, at least one component selected from the group (B) consisting of Nb and Ta, and at least one component selected from the group (D) consisting of Sn, Hf and Ge, and a/b (a and b denote the total
15 of molar fractions of the components A and B) ranges from 0.5 to 1.9. Thus, the present invention provides dielectric ceramics having a much higher unloaded Q value and a high dielectric constant, and is superior in thermo-stability at a resonant frequency.

The dielectric resonator of the present invention has a high unloaded Q value and a strong electrode layer.

In the foregoing, the ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component of each of the groups A, B and D is a phase in which both or either of Zr and Ti sites are (is) substituted with at least one of each
20 of the groups A, B and D. Basically, the ZrTiO_4 phase has an element ratio $\text{Zr/Ti} = 1$. Actually, also in a composition area where the element ratio is slightly shifted to the direction which is higher or lower than 1 (for example, in case Zr and Ti are soluble in the ZrTiO_4 phase), an area which can be regarded as the ZrTiO_4 constitution is present. Such an area is crystallographically referred to as a ZrTiO_4 phase.

25 Fig. 1A is a sectional view of a cylindrical coaxial dielectric resonator, which is axially cut off, according to an embodiment of the present invention.

Fig. 1B is a sectional view taken out along the line I-I shown in Fig. 1A.

Any compound such as oxide, carbonate, hydroxide, chloride, alkoxide of the component elements described above may be used as an initial material of the dielectric ceramic according to the present invention. As blending methods of
30 powdery raw materials, wet blending for mixing the materials with water or organic solvent in a ball mill and dry blending for mixing them by a mixer or a ball mill, etc. without using any solvent are generally known and any of these methods may be employed. Alternatively, the alkoxide method and coprecipitation method may be used depending on the initial materials. Because the process is thus comparatively uncomplicated, and a homogeneous mixture can be easily obtained, it is desirable to employ the wet blending method for mixing them in a ball mill by using a solvent, and a
35 dispersing agent may be additionally used for increasing the dispersing property of powders, or pH adjustment may be performed.

Although calcination of the mixture is not required, the sintering time can be reduced by calcination. Although the calcination temperature depends on the particular compositions, it is generally in the order of 1 to 8 hrs at about 700 to 1200°C.

40 As the milling method for the calcined material or mixture, any suitable method such as using a ball mill, high-speed rotor mill, media agitating mill and jet mill may be employed.

For molding, press molding is generally carried out to obtain a desired shape. Although not specifically limited, the pressure used in the press molding is generally in a range of approximately 0.5 to 2 tone/cm². A binder used for molding may be a binder used for molding ceramics, such as a polyvinyl alcohol binder, a polyvinyl butylal binder, an acrylic resin
45 binder or a wax binder. Although not specifically limited, the amount of the binder to be used is generally in a range of approximately 0.5 to 1 % by weight by solid matter conversion.

Although sintering is not specifically limited, as it depends on the particular compositions and dimensions of the moldings, it is generally desirable to perform firing at a temperature of approximately 400 to 700°C for about 1 to 24 hrs in order to remove binders, and then, at approximately 1100 to 1650°C for about 2 to 100 hrs.

50 An example of a cylindrical coaxial dielectric resonator will be described with reference to the drawings. Fig. 1A is a sectional view of the cylindrical coaxial dielectric resonator which is axially cut off, in which electrodes 1 and 4 are continuously formed on the surface of a cylindrical dielectric ceramic 2. The electrode is not formed on the surface of an opening end 3. Fig. 1B is a sectional view taken along the line I-I shown in Fig. 1A. According to the cylindrical coaxial dielectric resonator, electromagnetic waves are incident in the direction of the opening end 3, and the resonance (TEM mode) of the electromagnetic waves in a specific frequency area is utilized to obtain the necessary output from the
55 electrodes 1 and 4.

The present invention will be described with reference to the following examples.

Example 1

As initial materials, ZrO_2 , TiO_2 , MgO , CoO , ZnO , NiO , Nb_2O_5 , Ta_2O_5 , $MnCO_3$, $BaCO_3$, $SrCO_3$, $CaCO_3$, CuO , Bi_2O_3 , WO_3 , SnO_2 , HfO_2 and GeO_2 of high chemical purity (more than 98wt.%) were used, weighed so as to make predetermined compositions and wet-blended with ethanol by using a ball mill. The volume ratio between the powder and ethanol was approximately 2:3.

The mixture was removed from the ball mill, dried, and calcined for 2 hrs at $1000^\circ C$ in the air. The calcined product was wet-milled in the ball mill with ethanol. After the milled slurry was removed from the ball mill and dried, the powder was mixed with 8 % by weight of polyvinyl alcohol solution of 6 vol.% in concentration as a binder, homogenized, and granulated by sieving through a 32 mesh screen. The granulated powder was molded into a disk of 7 mm in diameter and approximately 3 mm in thickness by using molds and an oil hydraulic press at a molding pressure of 1.3 ton/cm^2 .

The molding was placed in a magnesia vessel of high purity, kept in the air at a temperature of $600^\circ C$ for 4 hrs to remove binders, then retained in the air at 1200 to $1500^\circ C$ for 24 hrs for sintering, and quenched (taken out of a furnace and air-cooled) or slowly cooled down to $1000^\circ C$ (at a cooling rate of $20^\circ C/hr$) thereafter, and dielectric ceramics were obtained.

The resonant frequency was obtained from measurement by the dielectric rod resonator method. The temperature coefficient at a resonant frequency τ_f was obtained in a range between $-25^\circ C$ and $85^\circ C$.

The compositions of main components and the amount of accessory components, which are to be added, of the dielectric ceramics thus produced are shown in Tables 1 and 2, respectively. Cooling conditions after sintering and a temperature coefficient at a resonant frequency (ppm/ $^\circ C$) are shown in Table 3. In Tables 1 to 3, comparative examples have an asterisk.

TABLE 1

25

TABLE 1

<u>Sample</u>		<u>Composition (molar fraction)</u>											
<u>No.</u>		<u>Zr</u>	<u>Ti</u>	<u>Mg</u>	<u>Co</u>	<u>Zn</u>	<u>Ni</u>	<u>Mn</u>	<u>Nb</u>	<u>Ta</u>	<u>Sn</u>	<u>Hf</u>	<u>Ge</u>
30	*1,*2	0.50	0.50	0	0	0	0	0	0	0	0	0	0
	3,4	0.35	0.50	0.05	0	0	0	0	0.10	0	0	0	0
35	5,6	0.35	0.50	0	0.05	0	0	0	0.10	0	0	0	0
	7,8	0.35	0.50	0.01	0.01	0.01	0.01	0.01	0.10	0	0	0	0
	9,10	0.35	0.50	0.01	0.01	0.01	0.01	0.01	0.10	0	0	0	0

11,12 0.35 0.50 0.01 0.01 0.01 0.01 0.01 0.10 0 0 0
 5 13,14 0.35 0.50 0.01 0.01 0.01 0.01 0.01 0.05 0.05 0 0
 *15*16 0.40 0.50 0 0 0 0 0 0 0.10 0 0
 10 *17*18 0.32 0.50 0 0.03 0 0 0 0.05 0 0.10 0
 19,20 0.35 0.50 0.01 0.01 0.01 0.01 0.01 0.05 0.05 0.01 0
 21,22 0.35 0.50 0.01 0.01 0.01 0.01 0.01 0.05 0.05 0 0.01
 15 23,24 0.35 0.50 0.01 0.01 0.01 0.01 0.01 0.05 0.05 0 0.01
 25,26 0.35 0.50 0.01 0.01 0.01 0.01 0.01 0.05 0.05 0.01 0.01

TABLE 2

Sample No.	Amount of additive (wt.%)					
	Ba	Sr	Ca	Cu	Bi	W
*1,*2	0	0.1	0	0	0	0
3,4	0	0.1	0	0	0	0
5,6	0.1	0	0	0	0	0
7,8	0	0	0	0	0.1	0
9,10	0	0	0	0.1	0	0
11,12	0	0	0	0	0	0.1
13,14	0.1	0.1	0.1	0.1	0	0
*15*16	0	0	0	0	0	0
*17*18	0	0	0	0	0	0
19,20	0.1	0.1	0.1	0.1	0	0
21,22	0.1	0	0	0	0	0
23,24	0	0.1	0	0	0	0
25,26	0.1	0.1	0.1	0.1	0	0

TABLE 3

Sample No.	Cooling condition after sintering	τ_f (ppm/°C)
*1	Quenching	58.9
*2	Slow cooling	59.1
3	Quenching	8.2
4	Slow cooling	8.9
5	Quenching	5.5
6	Slow cooling	4.8
7	Quenching	9.4
8	Slow cooling	9.3
9	Quenching	9.7
10	Slow cooling	10.1
11	Quenching	9.8
12	Slow cooling	9.6
13	Quenching	9.8
14	Slow cooling	9.7
*15	Quenching	-5.7
*16	Slow cooling	1.2
*17	Quenching	-22.5
*18	Slow cooling	-16.3
19	Quenching	5.8
20	Slow cooling	4.2
21	Quenching	0.9
22	Slow cooling	1.2
23	Quenching	9.5
24	Slow cooling	9.9
25	Quenching	8.5
26	Slow cooling	9.7

As recognized from the results shown in Table 3, in dielectric ceramics of sample Nos. 3 to 14 and 19 to 26 of the present example, the variation of temperature coefficient at a resonant frequency due to the heating history during sintering of $ZrTiO_4$ and ZrO_2 - SnO_2 - TiO_2 ceramics is reduced.

Example 2

As initial materials, ZrO_2 , TiO_2 , MgO , CoO , ZnO , NiO , $MnCO_3$, Nb_2O_5 , Ta_2O_5 , $BaCO_3$, $SrCO_3$, $CaCO_3$, CuO , Bi_2O_3 , and WO_3 of high chemical purity which are the same as in Example 1 were used, weighed so as to make a predetermined compositions and wet-blended with ethanol by using a ball mill. The volume ratio between the powder and ethanol was approximately 2:3.

The mixture was removed from the ball mill, dried, and calcined for 2 to 8 hrs at 800 to 1250°C in the air. The calcined product was wet-milled in the ball mill with ethanol. After the milled slurry was removed from the ball mill and dried, the powder was mixed with 8 % by weight of polyvinyl alcohol solution of 6 vol.% in concentration added thereto as a binder, homogenized, and granulated by sieving through 32 mesh screen. The granulated powder was molded into a disk of 7

mm in diameter and approximately 3 mm in thickness by using molds and an oil hydraulic press at a molding pressure of 1.3 ton/cm².

The molding was placed in a magnesia vessel of high purity, kept in the air at a temperature of 400 to 700°C for 4 to 8 hrs to remove binders, retained in the air at 1200°C to 1650°C for 1 to 100 hrs for sintering, and dielectric ceramics were obtained.

The resonant frequency, unloaded Q (Q_u) value and dielectric constant ϵ_r were obtained from measurement by the dielectric rod resonator method. The temperature coefficient at a resonant frequency τ_f was obtained in a range between -25°C and 85°C. The resonant frequency was obtained in a range between 4GHz and 12GHz.

The compositions of main components and the amount of accessory components, which are to be added, of the dielectric ceramics thus produced are shown in Table 4. The dielectric constant thus obtained, the temperature at a resonant frequency τ_f (ppm/°C) and the unloaded Q value are shown in Table 5. In Tables 4 and 5, comparative examples have an asterisk.

TABLE 4

Sample No.	A	B	Composition of main component				Accessory	
			(molar fraction)		(value)		component (wt.%)	
			<u>x</u>	<u>y</u>	<u>z</u>	<u>u</u>		
*27	Mg	Nb	0.400	0.150	0.450	0	Sr	0.005
*28	Co	Nb	0.400	0.150	0.450	0	Sr	0.005
*29	Zn	Nb	0.400	0.150	0.450	0	Ba	0.005
*30	Ni	Nb	0.400	0.150	0.450	0	Ca	0.005
31	Mg	Nb	0.200	0.200	0.600	0	Sr	1.000
32	Co	Nb	0.200	0.200	0.600	0	Sr	1.000
33	Ni	Nb	0.200	0.200	0.600	0	Sr	1.000

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	34	Mg	Nb	0.450	0.200	0.350	0	Sr	0.500
5	35	Co	Nb	0.450	0.200	0.350	0	Sr	0.500
	36	Mg	Nb	0.200	0.600	0.200	0	Ba	0.500
10	37	Zn	Nb	0.200	0.600	0.200	0	Ba	0.500
	*38	Mg	Nb	0.150	0.700	0.150	0	Sr	1.000
	*39	Mg	Nb	0.150	0.120	0.730	0	Ba	0.500
15	40	Mg	Nb	0.100	0.200	0.700	0	Ba	0.500
	41	Ni	Nb	0.100	0.200	0.700	0	Ba	0.500
20	*42	-	-	0.550	0.450	0	0	-	0
	43	Mg	Nb	0.490	0.500	0.010	0	Ba	0.005
	44	Co	Nb	0.490	0.500	0.010	0	Ba	0.005
25	45	Zn	Nb	0.490	0.500	0.010	0	Ba	0.005
	46	Ni	Nb	0.490	0.500	0.010	0	Ba	0.005
30	47	Mg	Nb	0.300	0.300	0.400	0	Sr	1.000
	48	Mg	Nb	0.400	0.400	0.200	0	Sr	0.005
	49	Co	Nb	0.400	0.400	0.200	0	Sr	0.005
35	50	Zn	Nb	0.400	0.400	0.200	0	Sr	0.005
	51	Mg	Nb	0.340	0.520	0.140	0	Sr	0.100
40	52	Co	Nb	0.340	0.520	0.140	0	Sr	0.100
	53	Zn	Nb	0.340	0.520	0.140	0	Sr	0.100
	54	Ni	Nb	0.340	0.520	0.140	0	Sr	0.100
45	55	Mg	Nb	0.450	0.450	0.100	0	Sr	0.100
	*56	Mg	Nb	0.650	0.200	0.100	0	Ca	0.100
50	*57	Co	Nb	0.650	0.200	0.100	0	Ca	0.100
	58	Mg	Nb	0.600	0.300	0.100	0	Ca	0.100
55	59	Mg	Nb	0.100	0.400	0.500	0	Bi	0.100

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	60	Ni	Nb	0.100	0.400	0.500	0	Bi	0.100
5	*61	Mg	Nb	0.050	0.500	0.450	0	Ca	0.100
	*62	Co	Nb	0.050	0.500	0.450	0	Si	0.100
10	63	Mg	Nb	0.450	0.350	0.200	0	Sr	1.000
	64	Mg	Nb	0.350	0.450	0.200	0	Sr	1.000
								Cu	0.005
15	65	Mg	Nb	0.350	0.450	0.200	0	Sr	1.000
								Cu	0.100
20	66	Mg	Nb	0.350	0.450	0.200	0	Sr	1.000
								W	0.005
	67	Mg	Nb	0.350	0.450	0.200	0	Sr	1.000
25								W	0.100
	68	Mg	Nb	0.350	0.450	0.200	0	Sr	1.000
30								W	1.000
	69	Mg	Nb	0.350	0.450	0.200	0	Sr	1.000
								W	2.000
35	70	Mg	Nb	0.350	0.450	0.200	0	Sr	1.000
	71	Mg	Nb	0.350	0.450	0.200	0.01	Sr	1.000
40	72	Co	Nb	0.350	0.450	0.200	0.01	Sr	1.000
	73	Zn	Nb	0.350	0.450	0.200	0.01	Sr	1.000
	74	Ni	Nb	0.350	0.450	0.200	0.01	Sr	1.000
45	75	Mg	Nb	0.350	0.450	0.200	0.05	Sr	1.000
	76	Mg	Nb	0.350	0.450	0.200	0.20	Sr	1.000
50	77	Co	Nb	0.350	0.450	0.200	0.20	Sr	1.000
	78	Mg	Nb	0.350	0.450	0.200	0.50	Sr	1.000
55	79	Mg	Nb	0.350	0.450	0.200	1.00	Sr	1.000

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	80	Mg	Nb	0.350	0.450	0.200	1.90	Sr 1.000
5	81	Co	Nb	0.350	0.450	0.200	1.90	Sr 1.000
	82	Mg	Nb	0.350	0.450	0.200	2.00	Sr 1.000
10	83	Mg _{1/4} Co _{1/4}	Nb	0.340	0.520	0.140	0	Sr 0.100
		Zn _{1/4} Ni _{1/4}						
	84	Mg _{1/2} Co _{1/2}	Nb	0.340	0.520	0.140	1.00	Sr 0.100
15	85	Mg _{1/3} Co _{1/3}	Ta	0.340	0.520	0.140	1.00	Sr 0.100
		Ni _{1/3}						
20	86	Mg _{1/4} Co _{1/4}	Nb _{1/2}	0.340	0.520	0.140	1.00	Sr 0.100
		Zn _{1/4} Ni _{1/4}	Ta _{1/2}					
	87	Mg _{39/40}	Nb _{1/2}	0.340	0.520	0.140	0.02	Bi 0.100
25		Mn _{1/40}	Ta _{1/2}					
	88	Mg _{113/200}	Nb	0.328	0.502	0.170	0.41	Bi 0.100
30		Mn _{87/200}						
	89	Mn	Nb	0.200	0.600	0.200	0	Ca 0.100
	90	Mg	Nb	0.300	0.400	0.300	1.00	Sr 0.500
35	91	Mg	Nb	0.300	0.400	0.300	1.00	Ba 0.500
	92	Mg	Nb	0.300	0.400	0.300	1.00	Ca 0.500
40	93	Mg	Nb	0.300	0.400	0.300	1.00	Bi 0.500
	94	Mg	Nb	0.300	0.400	0.300	1.00	Ba 0.500
								Sr 0.500
45								Ca 0.500
								Bi 0.500
50	95	Mg	Nb	0.300	0.400	0.300	1.00	Sr 1.500
	96	Mg	Nb	0.300	0.400	0.300	1.00	Sr 3.000
55	97	Mg	Nb	0.300	0.400	0.300	1.00	Sr 7.000

*98 Mg Nb 0.300 0.400 0.300 1.00 Sr 8.000

5

TABLE 5

	<u>Sample No.</u>	<u>ε_r</u>	<u>τ_f</u>	<u>Qu</u>
10	*27	30.1	-84.9	950
	*28	29.9	-70.5	850
15	*29	30.0	-88.7	970
	*30	30.8	-69.4	830
20	31	32.5	-10.8	8000
	32	31.3	-8.9	9000
	33	30.9	-7.8	8100
25	34	32.3	-32.1	4300
	35	33.1	-19.5	4800
30	36	57.5	47.4	5300
	37	55.5	40.2	6100
	*38	75.8	225.2	370
35	*39	28.0	-84.8	980
	40	33.8	-8.5	9600
40	41	26.8	-5.4	9600
	*42	45.8	250.8	1800
	43	44.5	42.3	3900
45	44	44.3	42.0	3600
	45	43.8	45.9	3100
50	46	44.5	46.8	3100
	47	39.3	15.3	6000
55	48	42.0	0.3	9700

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	49	43.1	12.1	8500
5	50	42.2	-5.3	8300
	51	43.1	9.3	7900
10	52	45.1	13.4	5100
	53	44.1	1.3	7900
	54	42.9	16.2	5100
15	55	41.5	10.3	5500
	*56	35.7	60.5	870
20	*57	29.5	21.3	620
	58	40.2	45.9	4000
	59	65.5	48.9	3300
25	60	55.8	48.1	4100
	*61	82.9	151.8	830
30	*62	86.8	213.3	420
	63	42.8	14.3	4800
	64	45.6	20.0	4700
35	65	43.7	28.7	4000
	66	45.7	19.5	4900
40	67	42.9	16.3	4600
	68	40.2	7.3	4200
	69	37.1	4.2	4000
45	70	45.8	19.7	4700
	71	44.5	14.1	4900
50	72	47.0	35.4	4700
	73	43.7	19.8	5100
55	74	44.2	40.2	4700

	75	42.7	14.0	5100
5	76	43.8	10.5	6700
	77	45.2	30.4	7100
10	78	42.9	9.3	7200
	79	41.5	8.5	7500
	80	35.2	0.1	6000
15	81	32.3	-9.8	5200
	82	34.2	-5.3	4300
20	83	45.1	17.3	5700
	84	43.8	6.7	7500
	85	40.1	9.8	8500
25	86	41.8	4.9	7300
	87	43.4	9.8	7200
30	88	42.9	8.7	6800
	89	61.2	48.5	3500
	90	41.2	-25.8	8500
35	91	40.3	-35.7	9200
	92	40.7	-36.4	6300
40	93	44.3	-24.1	5800
	94	42.5	-34.2	4900
	95	42.8	-17.5	8100
45	96	44.5	-3.2	7000
	97	52.1	38.5	3800
50	*98	59.3	58.3	910

As is apparent from the results shown in Table 5, in dielectric ceramic compositions within a composition range of the invention, the dielectric constant is kept at a high value at microwave frequencies, while a high unloaded Q value is provided.

On the contrary, when X is higher than 0.60, the unloaded Q value is significantly reduced as observed in sample Nos. 56 and 57. The objects of the invention cannot readily be achieved. When x is lower than 0.10, the unloaded Q value is reduced as observed in Example Nos. 61 and 62.

When y is higher than 0.60, the unloaded Q value is significantly reduced as observed in sample No. 38. Further, when y is lower than 0.20, the unloaded Q value is significantly reduced as observed in sample Nos. 27 to 30 and No. 39. Consequently, the objects of the invention cannot readily be achieved.

When z is higher than 0.70, the unloaded Q value is reduced as observed in sample No. 39. Further, when z is lower than 0.01, the unloaded Q value is reduced as observed in sample No. 42. Consequently, the objects of the invention cannot readily be achieved.

Additionally, the unloaded Q value can be improved by increasing u to a higher value than 0. However, when u exceeds 1.90, the unloaded Q value is reduced as observed in sample No. 82. Also in the case of sample No. 82, the properties were better than those of conventional dielectric ceramics.

When the amount of accessory component to be added is higher than 7.000 % by weight, the unloaded Q value is significantly reduced as observed in sample No. 98. Consequently, the objects of the invention cannot readily be achieved.

It was confirmed within the composition range of the example that the unloaded Q value was improved by using A, which is at least one element selected from Mg, Co, Zn, Ni, and Mn and B, which is at least one element selected from Nb and Ta, oxides were calcined in advance at a temperature of 800 to 1200°C.

Additionally, a ZrTiO_4 phase or one recognized as being a crystallographical ZrTiO_4 phase was confirmed by powder X-ray diffraction of a dielectric ceramic within the composition range of Examples 1 and 2 of the invention. It was further confirmed in composition analysis by a local X-ray diffractometer of a fracture surface and polished surface of the dielectric ceramic having, as the main component, ZrTiO_4 phase or crystallographical ZrTiO_4 phase that all components of Zr, Ti, A and B (wherein A is at least one component selected from Mg, Co, Zn, Ni and Mn, and B is at least one component selected from Nb and Ta) were present in a single grain, and their composition ratio was consistent with the composition ratio between other grains that constitute the main phase in the same dielectric ceramic. It was also confirmed that all components A and B blended were present in a single grain. Moreover, it was confirmed that a dielectric ceramic with components Zr, Ti, A and B present in a grain which constitutes the main phase showed a higher lattice constant in comparison with ZrTiO_4 ceramic obtained under the same sintering conditions. Accordingly, it was confirmed that components A and B are substituted in the ZrTiO_4 phase or the crystallographical ZrTiO_4 phase.

Such dielectric ceramics specifically showed a high unloaded Q value and a high dielectric constant, and were superior in thermo-stability at a resonant frequency. The unloaded Q value was even higher when the molar ratio a/b of the component A to the component B was 0.5 or more and 1.9 or less.

As is apparent from the results described above, it was confirmed that the dielectric ceramics of the example are capable of maintaining the dielectric constant at a high value at microwave frequencies, while providing a high unloaded Q value, and are superior in thermo-stability at a resonant frequency.

Example 3

As initial materials, ZrO_2 , TiO_2 , MgO , CoO , ZnO , NiO , MnCO_3 , Nb_2O_5 , Ta_2O_5 , SnO_2 , HfO_2 , GeO_2 , BaCO_3 , SrCO_3 , CaCO_3 , CuO , Bi_2O_3 , and WO_3 of high chemical purity which are the same as in Example 1 were used, weighed so as to make predetermined compositions and wet-blended with ethanol by using a ball mill. The volume ratio between the powder and ethanol was approximately 2:3.

The mixture was removed from the ball mill, dried, and calcined for 2 to 8 hrs at 800°C to 1250°C in the air. The calcined product was wet-milled in the ball mill with ethanol. After the milled slurry was removed from the ball mill and dried, the powder was mixed with 8 % by weight of polyvinyl alcohol solution of 6 vol.% in concentration added thereto as a binder, homogenized, and granulated by sieving through a 32 mesh screen. The granulated powder was molded into a disk of 7 mm in diameter and approximately 3 mm in thickness by using molds and an oil hydraulic press at a molding pressure of 1.3 ton/cm².

The molding was placed in a magnesia vessel of high purity, kept in the air at a temperature of 400°C to 700°C for 4 to 8 hrs to remove binders, retained in the air at 1200°C to 1650°C for 1 to 100 hrs for sintering, and dielectric ceramics were obtained.

The resonant frequency, unloaded Q (Q_u) value and dielectric constant ϵ_r were obtained from measurement by the dielectric rod resonator method. The temperature coefficient at a resonant frequency τ_f was obtained in a range between -25°C and 85°C. The resonant frequency was obtained in a range between 4 GHz and 12GHz.

The compositions of main components and the amount of accessory components, which are to be added, of the dielectric ceramics thus produced are shown in Table 6. The dielectric constant thus obtained, the temperature at a resonant frequency τ_f (ppm/°C) and the unloaded Q value are shown in Table 7. In Tables 6 and 7, comparative examples have an asterisk.

TABLE 6

5	Sample No.	A	B	D	Composition of main component					Accessory component	
					(molar fraction)		(value)				
					<u>x</u>	<u>y</u>	<u>z</u>	<u>v</u>	<u>u</u>	(wt.%)	
10	*99	Mg	Nb	Sn	0.400	0.150	0.400	0.050	0	Sr	0.005
	100	Mg	Nb	Sn	0.200	0.200	0.400	0.200	0	Sr	1.000
15	101	Co	Nb	Sn	0.200	0.200	0.400	0.200	0	Sr	1.000
	102	Ni	Nb	Sn	0.200	0.200	0.400	0.200	0	Sr	1.000
20	103	Mg	Nb	Sn	0.450	0.200	0.300	0.050	0	Sr	0.500
	104	Co	Nb	Sn	0.450	0.200	0.300	0.050	0	Sr	0.500
	105	Mg	Nb	Sn	0.200	0.600	0.100	0.100	0	Ba	0.500
25	106	Zn	Nb	Sn	0.200	0.600	0.150	0.050	0	Ba	0.500
	*107	Mg	Nb	Sn	0.150	0.700	0.100	0.050	0	Sr	1.000
30	*108	Mg	Nb	Sn	0.150	0.120	0.530	0.200	0	Ba	0.500
	109	Mg	Nb	Sn	0.100	0.200	0.500	0.200	0	Ba	0.500
	*110	Mg	Nb	Sn	0.100	0.200	0.300	0.400	0	Ba	0.500
35	*111	-	-	-	0.550	0.450	0	0	0	-	0
	112	Mg	Nb	Sn	0.490	0.450	0.010	0.050	0	Ba	0.005
40	113	Mg	Nb	Sn	0.300	0.300	0.300	0.100	0	Sr	1.000
	114	Mg	Nb	Sn	0.400	0.400	0.199	0.001	0	Sr	0.005
	115	Co	Nb	Sn	0.400	0.400	0.199	0.001	0	Sr	0.005
45	116	Zn	Nb	Sn	0.400	0.400	0.199	0.001	0	Sr	0.005
	117	Mg	Nb	Sn	0.450	0.450	0.050	0.050	0	Sr	0.100
50	*118	Mg	Nb	Sn	0.650	0.200	0.050	0.050	0	Ca	0.100
	119	Mg	Nb	Sn	0.600	0.300	0.050	0.050	0	Ca	0.100
55	*120	Mg	Nb	Sn	0.050	0.500	0.400	0.050	0	Ca	0.100

	121	Mg	Nb	Sn	0.450	0.350	0.150	0.050	0	Sr	1.000
5	122	Mg	Nb	Sn	0.350	0.450	0.150	0.050	0	Sr	1.000
										Cu	0.005
10	123	Mg	Nb	Sn	0.350	0.450	0.150	0.050	0	Sr	1.000
										Cu	0.100
	124	Mg	Nb	Sn	0.350	0.450	0.150	0.050	0	Sr	1.000
15										W	0.005
	125	Mg	Nb	Sn	0.350	0.450	0.150	0.050	0	Sr	1.000
										W	0.100
20	126	Mg	Nb	Sn	0.350	0.450	0.150	0.050	0	Sr	1.000
										W	1.000
25	127	Mg	Nb	Sn	0.350	0.450	0.150	0.050	0	Sr	1.000
										W	2.000
30	128	Mg	Nb	Sn	0.350	0.450	0.150	0.050	0	Sr	1.000
	129	Mg	Nb	Sn	0.350	0.450	0.150	0.050	0.01	Sr	1.000
	130	Mg	Nb	Sn	0.350	0.450	0.150	0.050	0.05	Sr	1.000
35	131	Mg	Nb	Sn	0.350	0.450	0.150	0.050	0.20	Sr	1.000
	132	Mg	Nb	Sn	0.350	0.450	0.150	0.050	0.50	Sr	1.000
40	133	Mg	Nb	Sn	0.350	0.450	0.150	0.050	1.00	Sr	1.000
	134	Mg	Nb	Sn	0.350	0.450	0.150	0.050	1.90	Sr	1.000
	135	Co	Nb	Sn	0.350	0.450	0.150	0.050	1.90	Sr	1.000
45	136	Mg	Nb	Sn	0.350	0.450	0.150	0.050	2.00	Sr	1.000
	137	Mg _{1/4}	Nb	Sn	0.340	0.520	0.130	0.010	0	Sr	0.100
50		Co _{1/4}									
		Zn _{1/4}									
55		Ni _{1/4}									

5	138	Mg _{1/3}	Ta	Sn	0.340	0.520	0.130	0.010	1.00	Sr	0.100
		Co _{1/3}									
		Ni _{1/3}									
10	139	Mg _{1/4}	Nb _{1/2}	Sn	0.340	0.520	0.130	0.010	1.00	Sr	0.100
		Co _{1/4}	Ta _{1/2}								
		Zn _{1/4}									
15		Ni _{1/4}									
	140	Mn	Nb	Sn	0.200	0.600	0.190	0.010	0	Ca	0.100
20	141	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr	0.500
	142	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Ba	0.500
	143	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Ca	0.500
25	144	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Bi	0.500
	145	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Ba	0.500
30										Sr	0.500
										Ca	0.500
										Bi	0.500
35	146	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr	1.500
	147	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr	3.000
40	148	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr	7.000
	*149	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr	8.000
45	150	Mg	Nb	Hf	0.350	0.450	0.150	0.050	1.90	Sr	1.000
	151	Mg	Nb	Ge	0.350	0.450	0.150	0.050	1.90	Sr	1.000

50

55

TABLE 7

	<u>Sample No.</u>	<u>ϵ_r</u>	<u>τ_f</u>	<u>Q_u</u>
5	*99	29.8	-85.3	1200
	100	27.6	-20.4	9600
10	101	26.7	-17.5	7500
	102	28.3	-15.4	6900
15	103	31.7	-34.0	4000
	104	32.9	-22.5	4100
	105	55.4	28.3	5500
20	106	53.1	15.3	5800
	*107	74.3	225.0	480
25	*108	21.3	-91.2	1200
	109	30.2	-14.5	8600
30	*110	24.3	-60.5	400
	*111	45.8	250.8	1800
	112	42.5	23.2	4800
35	113	37.2	7.8	6500
	114	41.5	-0.2	8300
40	115	43.0	11.5	7800
	116	42.0	-5.8	6800
	117	40.1	4.2	5100
45	*118	33.0	60.0	320
	119	40.1	42.3	3100
50	*120	82.3	147.2	200
	121	42.1	10.3	4100
55	122	43.1	15.5	4000

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	123	41.0	25.7	3800
5	124	43.1	15.1	4200
	125	40.9	11.9	4000
10	126	38.0	3.1	3700
	127	35.4	-1.0	3500
	128	43.2	15.3	4000
15	129	42.9	14.9	4500
	130	41.2	3.2	5000
20	131	40.5	0.2	6100
	132	37.2	-4.5	6300
	133	34.3	-15.5	7000
25	134	30.1	-32.5	7100
	135	30.9	-35.4	5800
30	136	28.9	-37.4	3900
	137	44.7	15.3	5100
	138	39.7	9.3	8100
35	139	40.9	4.5	6500
	140	60.3	44.9	3800
40	141	37.9	-30.3	7800
	142	36.1	-35.4	8100
	143	36.9	-35.1	5400
45	144	42.3	-25.9	3800
	145	40.1	-33.2	3500
50	146	39.3	-20.1	6900
	147	44.5	1.2	5800
55	148	50.2	39.5	4100

	*149	61.5	65.4	320
5	150	45.3	-28.5	5300
	151	30.9	-34.5	4900

10

As is apparent from the results shown in Table 7, it was confirmed that, in dielectric ceramic compositions within a composition range of the present invention, the dielectric constant is kept at a high value at microwave frequencies, while a high unloaded Q value is provided.

On the contrary, when X is higher than 0.60, the unloaded Q value is significantly reduced as observed in sample No. 118. Consequently, the objects of the invention cannot readily be achieved. When x is lower than 0.10, the unloaded Q value is reduced as observed in sample No. 120. Consequently, the objects of the invention cannot readily be achieved.

When y is higher than 0.60, the unloaded Q value is significantly reduced as observed in sample No. 107. Further, when y is lower than 0.20, the unloaded Q value is significantly reduced as observed in sample Nos. 99 and 108. Consequently, the objects of the invention cannot readily be achieved.

When z is higher than 0.50, the unloaded Q value is reduced as observed in sample No. 108. When z is lower than 0.01, the unloaded Q value is reduced as observed in sample No. 111. Consequently, the objects of the invention cannot readily be achieved.

Additionally, the unloaded Q value can be improved by increasing w to a higher value than 0. However, when w exceeds 1.90, the unloaded Q value is reduced as shown in sample No. 136. Also in the case of sample No. 136, the properties were better than those of conventional dielectric ceramics.

When the amount of accessory component to be added is higher than 7.000 % by weight, the unloaded Q value is significantly reduced as observed in sample No. 149. Consequently, the objects of the invention cannot readily be achieved.

It was confirmed within the composition range of the example that the unloaded Q value was improved by using A, which is at least one element selected from Mg, Co, Zn, Ni, and Mn and B, which is at least one element selected from Nb and Ta, oxides that were calcined in advance at a temperature of 800°C to 1200°C.

Additionally, a ZrTiO₄ phase or one recognized as being a crystallographical ZrTiO₄ phase was confirmed by powder X-ray diffraction of a dielectric ceramic within the composition range of Examples 1 and 3 of the invention. It was further confirmed in composition analysis by a local X-ray diffractometer of a fracture surface and polished surface of the dielectric ceramic having as the main component ZrTiO₄ phase or crystallographical ZrTiO₄ phase, that all components of Zr, Ti, A, B and D (wherein A is at least one component selected from Mg, Co, Zn, Ni and Mn, B is at least one component selected from Nb and Ta, and D is at least one component selected from Sn, Hf and Ge) were present in a single grain, and their composition ratio was consistent with the composition ratio between other grains that constitute the main phase in the same dielectric ceramic. It was also confirmed that all components A, B and D blended were present in a single grain.

Moreover, it was confirmed that a dielectric ceramic with components Zr, Ti, A, B and D present in a grain which constitutes the main phase showed a higher lattice constant in comparison with ZrTiO₄ ceramic obtained under the same sintering conditions. Accordingly, it was confirmed that components A, B and D are substituted in the ZrTiO₄ phase or the crystallographical ZrTiO₄ phase.

Such dielectric ceramics specifically showed a high unloaded Q value and a high dielectric constant, and were superior in thermostability at a resonant frequency. The unloaded Q value was even higher when the molar ratio a/b of the component A to the component B was 0.5 or more and 1.9 or less.

As is obvious from the results described above, it was confirmed that the dielectric ceramics of the example are capable of maintaining the dielectric constant at a high value at microwave frequencies, while providing a high unloaded Q value, and are superior in thermo-stability at a resonant frequency.

Example 4

As initial materials, ZrO₂, TiO₂, MgO, CoO, ZnO, NiO, MnCO₃, Nb₂O₅, Ta₂O₅, BaCO₃, SrCO₃, CaCO₃, CuO, Bi₂O₃, and WO₃ of high chemical purity were used, weighed so as to make predetermined compositions and wet-blended with ethanol by using a ball mill. The volume ratio between the powder and ethanol was approximately 2:3.

The mixture was removed from the ball mill, dried, and calcined for 2 to 8 hrs at 800°C to 1250°C in the air. The calcined product was wet-milled in the ball mill with ethanol. After the milled slurry was removed from the ball mill and dried, the powder was mixed with 8 % by weight of polyvinyl alcohol solution of 6 vol.% in concentration added thereto.

as a binder, homogenized, and granulated by sieving through 32 mesh screen. The granulated powder was molded into a cylindrical coaxial shape by using molds and an oil hydraulic press at a molding pressure of 1.3 ton/cm².

The molding was placed in a magnesia vessel of high purity, kept in the air at a temperature of 400°C to 700°C for 4 to 8 hrs to remove binders, retained in the air at 1200°C to 1650°C for 1 to 100 hrs for sintering, and cylindrical coaxial dielectric ceramics having an outer diameter of 7.2 mm and an inner diameter of 3.6 mm were obtained.

When copper was used for an electrode material, a copper coat having a thickness of about 3.5 μm was formed on the dielectric ceramic surface by the electroless plating method. When silver was used for the electrode material, silver paste which is on the market was burned to form a silver coat. In both cases, one of two end faces of the coaxial type device ground the electrode material, so that a TEM mode resonator was obtained.

The compositions of main components and the amount of accessory components, which are to be added, of the dielectric resonator thus produced are shown in Table 8, the electrode material which was used, the unloaded Q value and the bond strength are shown in Table 9. The resonant frequency was 1.3 to 1.7 GHz. In Tables 8 and 9, comparative examples have an asterisk.

TABLE 8

5	<u>Sample</u>		<u>A</u>	<u>B</u>	<u>Composition of main component</u>				<u>Accessory</u>	
	<u>No.</u>	<u>(molar fraction)</u>			<u>(value)</u>	<u>component(wt.%)</u>				
		<u>x</u>						<u>y</u>	<u>z</u>	
10					<u>x</u>	<u>y</u>	<u>z</u>	<u>u</u>		
	*152	Mg		Nb	0.340	0.520	0.140	0	-	0
	*153	-		-	0.550	0.450	0	0	-	0
15	154	Mg		Nb	0.340	0.520	0.140	0	Sr	0.100
	155	Co		Nb	0.340	0.520	0.140	0	Sr	0.100
	156	Zn		Nb	0.340	0.520	0.140	0	Sr	0.100
20	157	Ni		Nb	0.340	0.520	0.140	0	Sr	0.100
	158	Mg		Nb	0.100	0.400	0.500	0	Bi	0.100
25	159	Ni		Nb	0.100	0.400	0.500	0	Bi	0.100
	160	Mg		Nb	0.450	0.350	0.200	0	Sr	1.000
	161	Mg		Nb	0.350	0.450	0.200	0	Sr	1.000
30									Cu	0.005
	162	Mg		Nb	0.350	0.450	0.200	0	Sr	1.000
35									Cu	0.100
	163	Mg		Nb	0.350	0.450	0.200	0	Sr	1.000
									W	0.005
40	164	Mg		Nb	0.350	0.450	0.200	0	Sr	1.000
									W	0.100
45	165	Mg		Nb	0.350	0.450	0.200	0	Sr	1.000
									W	1.000

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5	166	Mg	Nb	0.350	0.450	0.200	0	Sr	1.000
								W	2.000
10	167	Mg	Nb	0.350	0.450	0.200	0	Sr	1.000
	168	Mg	Nb	0.350	0.450	0.200	0.05	Sr	1.000
	169	Mg	Nb	0.350	0.450	0.200	0.20	Sr	1.000
15	170	Co	Nb	0.350	0.450	0.200	0.20	Sr	1.000
	171	Mg	Nb	0.350	0.450	0.200	0.50	Sr	1.000
	172	Mg	Nb	0.350	0.450	0.200	1.00	Sr	1.000
20	173	Mg	Nb	0.350	0.450	0.200	1.90	Sr	1.000
	174	Co	Nb	0.350	0.450	0.200	1.90	Sr	1.000
	175	Mg _{1/3} Co _{1/3}	Ta	0.340	0.520	0.140	1.00	Sr	0.100
25		Ni _{1/3}							
	176	Mg _{1/4} Co _{1/4}	Nb _{1/2}	0.340	0.520	0.140	1.00	Sr	0.100
		Zn _{1/4} Ni _{1/4}	Ta _{1/2}						
30	177	Mg _{39/40}	Nb _{1/2}	0.340	0.520	0.140	0.02	Bi	0.100
		Mn _{1/40}	Ta _{1/2}						
	178	Mg _{113/200}	Nb	0.328	0.502	0.170	0.41	Bi	0.100
35		Mn _{87/200}							
	179	Mg	Nb	0.300	0.400	0.300	1.00	Ba	0.500
	180	Mg	Nb	0.300	0.400	0.300	1.00	Ca	0.500
40	181	Mg	Nb	0.300	0.400	0.300	1.00	Bi	0.500
	182	Mg	Nb	0.300	0.400	0.300	1.00	Ba	0.500
								Sr	0.500
45								Ca	0.500
								Bi	0.500
50	183	Mg	Nb	0.300	0.400	0.300	1.00	Sr	1.500
55									

	184	Mg	Nb	0.300	0.400	0.300	1.00	Sr	1.500
5	185	Mg	Nb	0.300	0.400	0.300	1.00	Sr	3.000
	186	Mg	Nb	0.300	0.400	0.300	1.00	Sr	7.000
10	*187	Mg	Nb	0.300	0.400	0.300	1.00	Sr	8.000

TABLE 9

	<u>Sample</u>	<u>Electrode</u>	<u>Qu</u>	<u>Bond strength</u>
	<u>No.</u>	<u>material</u>		<u>(kg/4mm²)</u>
15	*152	Cu	150	0.4
20	*153	Cu	Unmeasurable due to electrode peeling	
25	154	Cu	550	6.8
	155	Cu	520	6.4
30	156	Cu	500	6.3
	157	Cu	510	6.0
	158	Cu	530	6.1
35	159	Cu	500	6.3
	160	Cu	630	9.7
40	161	Cu	670	12.0
	162	Cu	650	12.0
	163	Cu	660	11.5
45	164	Cu	650	10.9
	165	Cu	620	10.7
50	166	Cu	600	11.0
	167	Cu	650	9.3
55	168	Cu	670	9.1

	169	Cu	690	9.5
5	170	Cu	670	9.1
	171	Cu	710	8.8
10	172	Cu	740	9.6
	173	Cu	750	9.0
	174	Cu	740	8.9
15	175	Cu	580	7.3
	176	Cu	620	9.1
20	177	Cu	640	7.8
	178	Cu	630	7.5
	179	Cu	640	9.7
25	180	Cu	530	6.1
	181	Cu	610	9.3
30	182	Cu	670	11.5
	183	Cu	750	10.4
	184	Ag	730	12.0
35	185	Cu	740	11.5
	186	Cu	680	12.0
40	*187	Cu	210	10.5

As is apparent from the results shown in Table 9, the dielectric resonators of the embodiment had a high bond strength also when an electroless copper electrode is used in the same way as a silver electrode. For this reason, the unloaded Q value is high in a microwave frequency band and the resonant frequency can be prevented from deviating due to electrode peeling so that electric characteristics are stable. In addition, the dielectric resonators of the invention are suitable for forming electrodes by copper plating, so that they are suitable for large scale production and manufacturing costs can be reduced.

Additionally, a ZrTiO_4 phase or one recognized as being a crystallographical ZrTiO_4 phase was confirmed by powder X-ray diffraction of a dielectric ceramic within the composition range of Example 4 of the invention. It was further confirmed in composition analysis by a local X-ray diffractometer of a fracture surface and polished surface of the dielectric ceramic having as the main component ZrTiO_4 phase or crystallographical ZrTiO_4 phase, that all components of Zr, Ti, A and B (wherein A is at least one component selected from Mg, Co, Zn, Ni and Mn, and B is at least one component selected from Nb and Ta) were present in a single grain, and their composition ratio was consistent with the composition ratio between other grains that constitute the main phase in the same dielectric ceramic. It was also confirmed that all components A and B blended were present in a single grain. Moreover, it was confirmed that a dielectric ceramic with components Zr, Ti, A and B present in a grain which constitutes the main phase showed a higher lattice constant in comparison

with ZrTiO₄ ceramic obtained under the same sintering conditions. Accordingly, it was confirmed that components A and B are substituted in the ZrTiO₄ phase or the crystallographical ZrTiO₄ phase.

Such dielectric ceramics specifically showed a high unloaded Q value and a high dielectric constant, and were superior in thermostability at a resonant frequency. The unloaded Q value was even higher when the molar ratio a/b of the component A to the component B was 0.5 or more and 1.9 or less. The dielectric resonators having such dielectric ceramics had an unloaded Q value which is specially high, and a high electrode bond strength.

As is obvious from the results described above, it was confirmed that the dielectric resonators of the example have the unloaded Q value which is specially high at a microwave frequency band. Moreover, the resonant frequency can be prevented from deviating due to electrode peeling. In addition, the dielectric resonators of the invention are suitable for forming electrodes by copper plating, so that they can be produced on a large scale and manufacturing costs can be reduced.

Example 5

As initial materials, ZrO₂, TiO₂, MgO, CoO, ZnO, NiO, MnCO₃, Nb₂O₅, Ta₂O₅, SnO₂, HfO₂, GeO₂, BaCO₃, SrCO₃, CaCO₃, CuO, Bi₂O₃, and WO₃ of high chemical purity which are the same as in Example 1 were used, weighed so as to make predetermined compositions and wet-blended with ethanol by using a ball mill. The volume ratio between the powder and ethanol was approximately 2:3.

The mixture was removed from the ball mill, dried, and calcined for 2 to 8 hrs at 800°C to 1250°C in the air. The calcined product was wet-milled in the ball mill with ethanol. After the milled slurry was removed from the ball mill and dried, the powder was mixed with 8 % by weight of polyvinyl alcohol solution of 6 vol.% in concentration added thereto as a binder, homogenized, and granulated by sieving through 32 mesh screen. The granulated powder was molded into a cylindrical coaxial shape by using molds and an oil hydraulic press at a molding pressure of 1.3 ton/cm².

The molding was placed in a magnesia vessel of high purity, kept in the air at a temperature of 400°C to 700°C for 4 to 8 hrs to remove binders, retained in the air at 1200°C to 1650°C for 1 to 100 hrs for sintering, and cylindrical coaxial dielectric ceramics having an outer diameter of 7.2 mm and an inner diameter of 3.6 mm were obtained.

When copper was used for an electrode material, a copper coat having a thickness of about 3.5 μm was formed on the dielectric ceramic surface by the electroless plating method. When silver was used for the electrode material, silver paste which is on the market was burned to form a silver coat. In both cases, one of two end faces of the coaxial type device ground the electrode material, so that a TEM mode resonator was obtained.

The compositions of main components and the amount of accessory components, which are to be added, of the dielectric resonator thus produced are shown in Table 10, the electrode material which was used, the unloaded Q value and the bond strength are shown in Table 11. The resonant frequency is 1.3 to 1.7 GHz.

TABLE 10

5	Sample	A	B	D	Composition of main component					Accessory	
					No.	(molar fraction)			(value)		component
						x	y	z	v	u	
10	188	Mg _{1/4}	Nb	Sn	0.340	0.520	0.130	0.010	0	Sr 0.100	
		Co _{1/4}									
15		Zn _{1/4}									
		Ni _{1/4}									
20	189	Mg _{1/3}	Ta	Sn	0.340	0.520	0.130	0.010	1.00	Sr 0.100	
		Co _{1/3}									
		Ni _{1/3}									
25	190	Mg _{1/4}	Nb _{1/2}	Sn	0.340	0.520	0.130	0.010	1.00	Sr 0.100	
		Co _{1/4}	Ta _{1/2}								
30		Zn _{1/4}									
		Ni _{1/4}									
	191	Mn	Nb	Sn	0.200	0.600	0.190	0.010	0	Ca 0.100	
35	192	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 0.500	
	193	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Ba 0.500	
40	194	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Ca 0.500	
	195	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Bi 0.500	
	196	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Ba 0.500	
45										Sr 0.500	
										Ca 0.500	
50										Bi 0.500	
	197	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 1.000	
55										Cu 0.005	

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5	198	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 1.000
										Cu 0.100
10	199	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 1.000
										W 0.005
15	200	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 1.000
										W 0.100
20	201	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 1.000
										W 1.000
25	202	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 1.000
										W 2.000
30	203	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 1.500
	204	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 1.500
35	205	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 3.000
	206	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 7.000
40	*207	Mg	Nb	Sn	0.300	0.400	0.200	0.100	1.00	Sr 8.000
	208	Mg	Nb	Hf	0.350	0.450	0.150	0.050	1.90	Sr 1.000
45	209	Mg	Nb	Ge	0.350	0.450	0.150	0.050	1.90	Sr 1.000

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TABLE 11

Sample No.	Electrode material	Qu	Bond strength (kg/4mm ²)
188	Cu	580	8.8
189	Cu	540	8.1
190	Cu	590	8.3
191	Cu	480	5.1
192	Cu	670	9.3
193	Cu	600	9.1
194	Cu	480	5.7
195	Cu	540	8.7
196	Cu	720	10.8
197	Cu	760	12.0
198	Cu	740	12.0
199	Cu	730	10.9
200	Cu	740	11.4
201	Cu	700	9.7
202	Cu	650	8.9
203	Cu	760	10.8
204	Ag	720	12.0
205	Cu	720	11.1
206	Cu	700	11.3
207	Cu	180	12.0
208	Cu	630	10.1
209	Cu	540	8.9

As is apparent from the results shown in Table 11, the dielectric resonators of the embodiment had a high bond strength also when an electroless copper electrode is used in the same way as a silver electrode. For this reason, the unloaded Q value is high in a microwave frequency band and the resonant frequency can be prevented from deviating due to electrode peeling so that electric characteristics are stable. In addition, the dielectric resonators of the invention are suitable for forming electrodes by copper plating, so that they are suitable for large scale production and manufacturing costs can be reduced.

Additionally, a ZrTiO₄ phase or one recognized as being a crystallographical ZrTiO₄ phase was confirmed by powder X-ray diffraction of a dielectric ceramic within the composition range of Example 5. It was further confirmed in composition analysis by a local X-ray diffractometer of a fracture surface and polished surface of the dielectric ceramic having as the main component ZrTiO₄ phase or crystallographical ZrTiO₄ phase that all components of Zr, Ti, A, B and D (wherein A is at least one component selected from Mg, Co, Zn, Ni and Mn, B is at least one component selected from Nb and Ta, and D is at least one component selected from Sn, Hf and Ge) were present in a single grain, and their composition ratio was consistent with the composition ratio between other grains that constitute the main phase in the same dielectric ceramic. It was also confirmed that all components A, B and D blended were present in a single grain. Moreover, it was confirmed that a dielectric ceramic with components Zr, Ti, A, B and D present in a grain which constitutes the main phase showed a higher lattice constant in comparison with ZrTiO₄ ceramics obtained under the same sintering conditions. Accordingly, it was confirmed that components A, B and D are substituted in the ZrTiO₄ phase or the crystallographical ZrTiO₄ phase.

Such dielectric ceramics specifically showed a high unloaded Q value and a high dielectric constant, and were superior in thermo-stability at a resonant frequency. The unloaded Q value was even higher when the molar ratio a/b of

the component A to the component B was 0.5 or more and 1.9 or less. The dielectric resonators having such dielectric ceramics had an unloaded Q value which is specially high, and a high electrode bond strength.

As is apparent from the results described above, it was confirmed that the dielectric resonators of the example have the unloaded Q value which is especially high at a microwave frequency band. Moreover, the resonant frequency can be prevented from deviating due to electrode peeling. In addition, the dielectric resonators of the invention are suitable for forming electrodes by copper plating, so that they can be produced on a large scale and manufacturing costs can be reduced.

Although a dielectric ceramic having a cylindrical coaxial shape was used in Examples 4 and 5 of the invention, it is not limited to such a shape. For example, in the case of a TEM mode resonator using a dielectric ceramic having a prismatic coaxial or stepped coaxial shape, a microstrip line resonator using a dielectric resonator which has a planar shape, or a triplate resonator, an unloaded Q value which is equivalent to or more than the conventional ones can be obtained. Thus, a dielectric resonator in which stability is high and manufacturing costs are reduced can be obtained.

According to the structure of the dielectric ceramic of the invention, the variation in temperature coefficient at a resonant frequency due to heat history during sintering of ZrTiO_4 and $\text{ZrO}_2\text{-SnO}_2\text{-TiO}_2$ ceramics can be reduced. In addition, a high unloaded Q value is provided, and the temperature coefficient at a resonant frequency can be changed as desired without reducing the dielectric constant.

Furthermore, according to the structure of the dielectric resonator of the invention, a dielectric resonator having a high unloaded Q value and a strong electrode layer can be obtained.

20 Claims

1. A dielectric ceramic comprising as the main component a complex oxide formed of both Zr and Ti, at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, and as the accessory components at least one component selected from the group (C) consisting of Ba, Sr, Ca, Cu, Bi and W.

2. The dielectric ceramic according to Claim 1, wherein the main component of the dielectric ceramic is expressed by the Formula: $x\text{ZrO}_2 - y\text{TiO}_2 - z\text{A}_{(1+u)/3}\text{B}_{(2-u)/3}\text{O}_2$, wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, B denotes at least one component selected from the group (B) consisting of Nb and Ta, and x, y, z and u are present within the range expressed by Formula 1, wherein x, y and z denote molar fractions and u denotes a value expressed by the Formula 1.

$$x + y + z = 1$$

$$0.10 \leq x \leq 0.60$$

$$0.20 \leq y \leq 0.60$$

$$0.01 \leq z \leq 0.70$$

$$0 \leq u \leq 1.90$$

Formula 1

3. The dielectric ceramic according to Claim 1, wherein the accessory components of the dielectric ceramic are present within the range of 0.005 to 7.000 % by weight based on the entire weight of the ceramic.

4. The dielectric ceramic according to Claim 2, wherein the main component comprises a ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta.

5. The dielectric ceramic according to Claim 2, wherein the main component comprises a ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, and a/b (a and b denote the total of molar fractions of the components A and B) ranges from 0.5 to 1.9.

6. The dielectric ceramic according to Claim 1, wherein the complex oxide of the main component further comprises at least one component selected from the group (D) consisting of Sn, Hf and Ge.

7. The dielectric ceramic according to Claim 6, wherein the main component of the dielectric ceramic is expressed by the Formula: $x\text{ZrO}_2 - y\text{TiO}_2 - z\text{A}_{(1+u)/3}\text{B}_{(2-u)/3}\text{O}_2 - v\text{DO}_2$, wherein A denotes at least one component selected from

the group (A) consisting of Mg, Co, Zn, Ni and Mn, B denotes at least one component selected from the group (B) consisting of Nb and Ta, and D denotes at least one component selected from the group (D) consisting of Sn, Hf and Ge, and x, y, z, v, and u are present within the range expressed by Formula 2, wherein x, y, z and v denote molar fractions and u denotes a value expressed by the Formula 2.

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$$x + y + z + v = 1$$

$$0.10 \leq x \leq 0.60$$

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$$0.20 \leq y \leq 0.60$$

$$0.01 \leq z \leq 0.50$$

$$0.001 \leq v \leq 0.20$$

15

$$0 \leq u \leq 1.90$$

Formula 2

8. The dielectric ceramic according to Claim 6, wherein the dielectric ceramic further comprises at least one accessory component selected from the group (C) consisting of Ba, Sr, Ca, Cu, Bi and W within the range from 0.005 to 7.000 % by weight based on the entire weight of the ceramic.
9. The dielectric ceramic according to Claim 7, wherein the main component comprises a ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, at least one component selected from the group (B) consisting of Nb and Ta, and at least one component selected from the group (D) consisting of Sn, Hf and Ge.
10. The dielectric ceramic according to Claim 7, wherein the main component comprises a ZrTiO_4 or crystallographical ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, at least one component selected from the group (B) consisting of Nb and Ta, and at least one component selected from the group (D) consisting of Sn, Hf and Ge, and a/b (a and b denote the total of molar fractions of the components A and B) ranges from 0.5 to 1.9.
11. A dielectric resonator comprising the dielectric ceramic according to any of Claims 1 to 10, and an electrode on the surface of the dielectric ceramic.
12. The dielectric resonator according to Claim 11, wherein the electrode is copper or silver.
13. The dielectric resonator according to Claim 12, wherein the electrode is copper.

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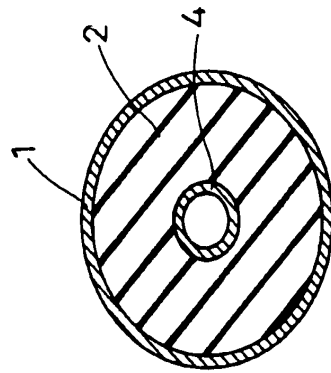


FIG. 1B

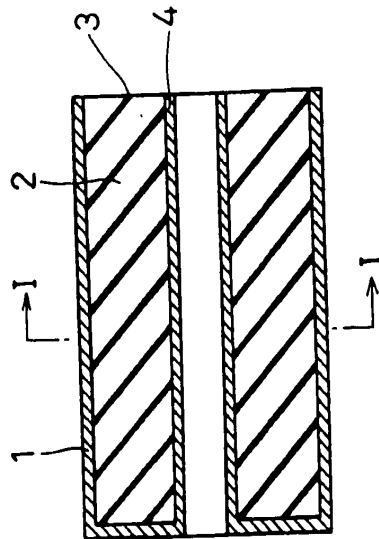


FIG. 1A



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EUROPEAN SEARCH REPORT

Application Number
EP 95 11 8228

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 587 140 (MATSUSHITA) * claims; examples *	1-13	C04B35/49 H01G4/12 H01B3/12
A	FR-A-2 581 639 (MURATA) * the whole document *	6-13	
X	DE-A-39 15 339 (SAKAI) * examples 2-4; tables 2-4 *	1,6	
A	DE-A-22 23 491 (BAYER AG) * claims 1-4,6; tables 2-4 *	1-5	
A	US-A-5 132 258 (H.TAKAHASHI ET AL.)		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C04B H01G H01B
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		4 March 1996	Harbron, J
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